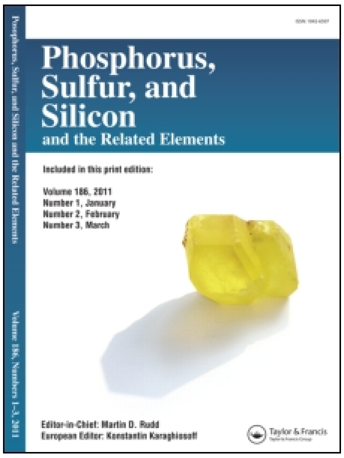

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Coordination Chemistry of Unsaturated Organophosphorus Ligands

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COORDINATION CHEMISTRY OF UNSATURATED ORGANOPHOSPHORUS LIGANDS

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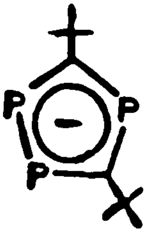
Abstract Similarities between phosphorus and carbon in unsaturated systems and their transition metal complexes are presented and discussed.

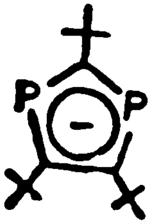
INTRODUCTION

The field of organotransition metal chemistry involving unsaturated organic ligands in which CH fragments are replaced by P is rapidly developing.[1] An extensive coordination chemistry of novel unsaturated organophosphorus compounds has recently been developed which parallels the better known organotransition metal compounds. A wide variety of metal complexes of phospha-alkynes, $RC\equiv P$, phosphaalkenes $R_2C=PR$, 1,3-diphosphacyclobutadiene, 1-phospha-allyl, 1,3-diphospha-allyl and mono- and di-phospha-allenes have recently been reported.[1,2]

Of special interest in view of the ubiquitous role that the cyclopentadienyl ligand has played in the development of organometallic



(I)



(II)

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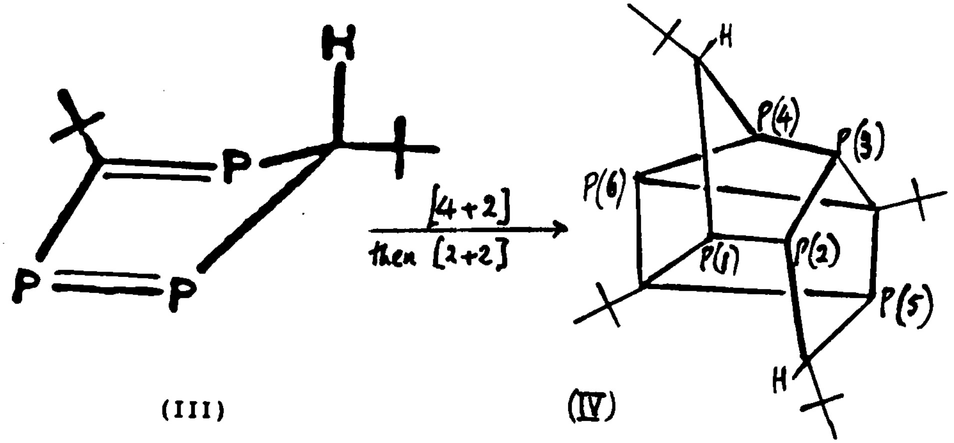
† In collaboration with Drs R. Bartsch, Dr M. F. Meidine, and Mr G. J. Sillet.

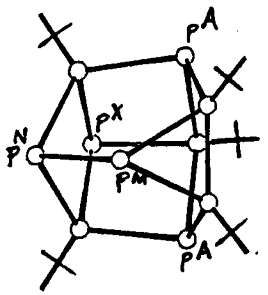
chemistry of transition metals is the use of the 1,2,4-triphosphacyclopentadienyl, $P_3C_2Bu^t_2$(I), and 1,3-diphosphacyclopentadienyl, $P_2C_3Bu^t_3$(II), rings in the synthesis of sandwich compounds of the type $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, (M = Cr,Fe)[3,4] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$,[3] $Ni(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^3\text{-}P_2C_3Bu^t_3)]$[5] and $[Co(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^4\text{-}P_3C_2Bu^t_2H)$.[6]

Careful protonation of the lithium salt of (I) in monoglyme with $EtOH/CH_3CO_2H$ affords $P_6C_4Bu^t_4H_2$(IV) which is the dimer of (III). The structure of (IV) which has been established by a single crystal X-ray diffraction study consists of a cage containing five directly bonded phosphorus atoms and no C-C bonds.[7]



(III) (IV)

Treatment of a 3:2 mixture of the lithium salts of (I) and (II)[8] with $FeCl_3$ or $CoBr_2$ gives rise to an oxidative coupling reaction of the two ring systems to afford the novel pentaphosphorus cage compound $P_5C_5Bu^t_5$(V).



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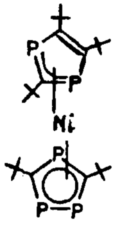


(VI)

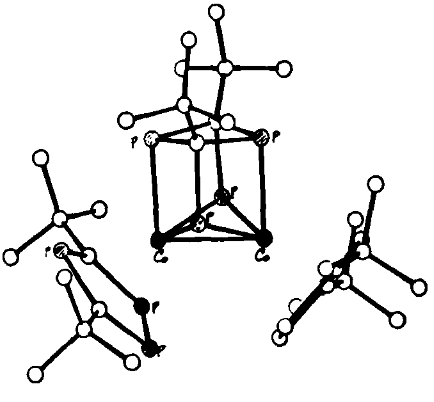
A single crystal X-ray structural determination reveals the cage molecular structure of (V), in which the five phosphorus atoms are part of two five-membered rings, three four-membered rings and one three-membered ring, respectively. The formation of a three-membered ring which could only result from P-P or P-C bond cleavage of the original ring systems (I) and (II) is remarkable. Unlike the hexaphosphorus cage compound (IV) in which five phosphorus atoms are joined together, no new P-P bond has been formed in (V), the only direct P-P bond obviously stemming from that of the original $P_3C_2Bu^t_2$ ring. All bond distances in (V) are similar to those found in (IV) being in the typical range of phosphorus-phosphorus, phosphorus-carbon and carbon-carbon single bonds.

The ^{31}P n.m.r. spectrum of (V) is almost first order and has been fully analysed and simulated as an A_2MNX spin system. The spectrum shows only one large $^1J_{PP}$ coupling (J_{MN}) which supports the X-ray diffraction study. The ^1H n.m.r. spectrum exhibits three singlets for the three inequivalent Bu^t groups as expected. The mass spectrum of (V) exhibits the parent ion at m/e = 500 and ions corresponding to the stepwise loss of Bu^t, Bu^tCP and P_2 fragments.

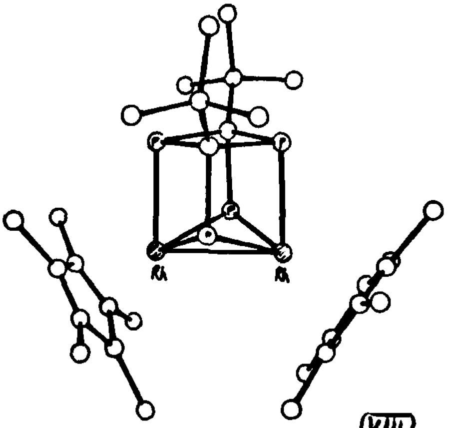
Treatment of a mixture of $Li(P_3C_2Bu^t_2)$ and $Li(P_2C_3Bu^t_3)$ with $[NiBr_2(monoglyme)_2]$ in monoglyme affords a low yield (ca. 5%) of the purple nickel complex $[Ni(P_3C_2Bu^t_2)(P_2C_3Bu^t_3)]$ (VI). No evidence was obtained for the formation of the paramagnetic 20e sandwich complexes $[Ni(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, $[Ni(\eta^3\text{-}P_2C_3Bu^t_3)_2]$ or $[Ni(\eta^5\text{-}P_2C_3Bu^t_3)(\eta^5\text{-}P_3C_2Bu^t_2)]$. The sharpness of the $^{31}P\{^1H\}$ n.m.r. spectra of (VI) which was fully analysed as an A_2BC_2 spin system is indicative of a dimagnetic 18e complex, suggesting that one ring is η^5-ligated and the other ring is η^3-bonded to the metal.

Other novel complexes to be reported and fully structurally characterised containing unusual cage structures are:

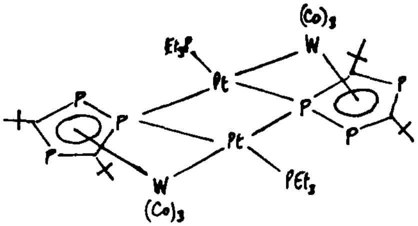
$[Co_2(P_4C_2Bu^t_2)(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (VII),[9] $[Rh_2(P_4C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)_2]$ (VIII),[10] the pentaphosphorus norbornadiene complex $[Rh(\eta^5\text{-}C_5Me_5)\text{-}(\eta^4\text{-}P_5C_2Bu^t_2(CHBu^tSiMe_3)]$[11] and $[Pt_2W_2(CO)_6(PEt_3)_2(P_3C_2Bu^t_2)_2]$ (IX). The latter is isolobally related to the analogous C_5H_5 complex but has a completely different structure,[12] because of the more basic nature of the $P_3C_2Bu^t_2$ ring.



(VII)



(VIII)



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